

Calculation of elastic properties

Crystal elasticity is characterized by a fourth-rank tensor, which is commonly expressed as a 6x6 matrix. The number of independent entries in this tensor is governed by the crystal symmetry. Apatites, with their hexagonal symmetry, exhibit five distinct elastic constants: $C_{11}, C_{12}, C_{13}, C_{33}$, and C_{44} . An additional dependent constant $C_{66} = (C_{11} - C_{12})/2$ also exists.

In Voigt notation ($xx \rightarrow 1, yy \rightarrow 2, zz \rightarrow 3, yz \rightarrow 4, xz \rightarrow 5, xy \rightarrow 6$), the equation is:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{pmatrix}$$

We use the stress-strain based approach to determine the independent elastic constants, since all of them can be calculated through three distinct types of imposed strains: (i) ϵ_1 , (ii) ϵ_3 and (iii) ϵ_4 .

All strains, except those deliberately imposed, are maintained at zero in this approach.

- Apply Strain ϵ_1 (**Basal Stretching**) A strain is applied only in the x-direction: $\epsilon = (\delta, 0, 0, 0, 0, 0)$. Substituting this into the matrix equation above yields the following stresses:

$$\sigma_1 = C_{11}\delta$$

$$\sigma_2 = C_{12}\delta$$

$$\sigma_3 = C_{13}\delta$$

Method: The simulation applies $\delta = \pm 0.0025$. It calculates the resulting stress σ_1 . The slope of the σ_1 vs. δ plot gives C_{11} . The slope of σ_2 vs. δ gives C_{12} .

- Apply Strain ϵ_3 (**Axial Stretching**) A strain is applied only in the c-axis direction: $\epsilon = (0, 0, \delta, 0, 0, 0)$. Substituting this into the matrix equation above yields the following stresses:

$$\sigma_3 = C_{33}\delta$$

$$\sigma_1 = C_{13}\delta$$

The slope of the σ_3 vs. δ plot gives C_{33} .

- Apply strain ϵ_4 : A strain is applied $\epsilon = (0, 0, 0, \delta, 0, 0)$. Substituting this into the matrix equation above yields the following stresses:

$$\sigma_4 = 2 * C_{44}\delta$$

The slope of the σ_4 vs. δ plot gives $2 * C_{44}$.

We now compare the single-crystal elastic constants obtained from our DFT calculations with the experimental data, wherever available.

To the best of our knowledge, there are no direct experimental studies on single-crystal elastic constants of HAP. So, we base all comparisons for HAP and FAP on the data used by Katz and Ukraincik.¹⁸ For CIAP, such a comparison could not be made due to the unavailability of experimental data.

The following general observations can be made from our results: (i) while the choice of XC is far more important than any other approximations, incorporating dispersion corrections changes the results, (ii) although small, the choice of PP can also alter the elastic constants by ~10% in some of the XCs, (iii) amongst all the independent elastic constants, C_{33} has the highest value, indicating the c axis to be the stiffest, and (iv) the obtained elastic constants satisfy the mechanical stability requirements for hexagonal structures:

$$C_{44} > 0, C_{11} - C_{12} > 0, C_{33}(C_{11} - C_{12}) - 2C_{13}^2 > 0;$$

Calculating Bulk Modulus (Voigt-Reuss-Hill)

Apart from elastic constants, another important elastic property is the isotropic bulk modulus (B), which measures the ability of a material to resist volumetric deformations.

We calculate B using the Voigt–Reuss–Hill (VRH) approximation, where the average of the Voigt (upper) and the Reuss (lower) bounds is taken as the isotropic bulk modulus: $B = (BV + BR)/2$.

- **Voigt Bound (V) - The Upper Limit** This assumes uniform strain throughout the crystal. The formula derived for hexagonal symmetry is:
- **Reuss Bound (R) - The Lower Limit** This assumes uniform stress throughout the crystal.
- **Final Bulk Modulus (B)** The reported value is the arithmetic mean of the two bounds.

The mathematical expression of Voigt (BV) and Reuss (BR) bounds are:

$$BV = 1/9[(2C_{11} + C_{33}) + 2 * (C_{12} + 2 * C_{13})]$$

$$BR = [(C_{11} + C_{12})C_{33} - 2 * C_{13}^2]/[C_{11} + C_{12} - 4 * C_{13} + 2 * C_{33}]$$

All three apatites show a consistent trend in B values: $FAP > HAP > CIAP$, which aligns with the observations in the literature. Since the constituting anion is the only difference between the three apatites, the trend may be explained from the standpoint of the equilibrated crystal volume. FAP (CIAP) with its smallest (largest) crystal volume has the largest (smallest) bulk modulus. Such an inverse relationship has been established for other

materials that belong to the same class, have similar crystal structure and bonding properties. However, under some of the XC functionals such as PBE-D3 and r2SCAN the trend is broken.

Lattice Parameters in Apatites

The apatites studied (HAP, FAP, CIAP) have a hexagonal crystal structure belonging to the space group $P6_3/m$.

In a hexagonal unit cell, the geometry is defined by two lattice parameters:

a (and b): The length of the basal axes, where $a = b$.

c: The length of the axis perpendicular to the basal plane

Density Functional Theory (DFT) approximations predict these lengths compared to experimental data.

- **Performance of Functionals:** Standard functionals like PBE tend to overestimate the lattice parameters (especially a) by up to 1.5%. PBEsol, which is optimized for solids, performs much better with deviations less than 0.5% for HAP and FAP.
- **Dispersion Corrections:** Adding van der Waals (vdW) dispersion corrections generally improves accuracy because it captures long-range attractive forces that standard functionals miss. The optB86b-vdW functional was found to be the most accurate overall.
- **The CIAP Anomaly:** Chlorapatite (CIAP) showed the highest deviation in lattice parameters. This is likely due to the specific positions of the Chloride ions, which have different fractional coordinates along the c-axis compared to the anions in HAP and FAP.

The Process:

- **Initial Guess:** Start with experimental crystal data (atomic coordinates) as a guess.
- **Optimization Loop:** The simulation adjusts the cell dimensions (a and c) and moves the atoms inside the cell. At each step, it calculates the forces on the atoms and the pressure on the cell.

- Convergence: The parameters are considered "found" when the total energy is minimized, and the atomic forces and pressure drop below a strict threshold (e.g., 0.2 kbar pressure)